Hence $\phi_0 V$ is a quantity which can only increase with the time and may be regarded as the entropy of the universe. This quantity proves to be equivalent to the expression that Lenz took for the entropy of the Einstein universe, but, in general, the expression for the entropy of a system in a gravitational field does not reduce to so simple a form.

[1] Tolman, R. C., these PROCEEDINGS, 14, No. 3, 268–272 (1928).

[2] Lenz, W., *Physik. Z.*, 27, 642–645 (1926).

[3] Einstein, A., *Berl. Ber.*, 448–459 (1918).

[4] See Eddington, A. S., *The Mathematical Theory of Relativity*, Cambridge, 1923, equations (69.21) and (69.22).

[5] See Eddington, l. c., equation (54.71).

[6] See Eddington, l. c., equations (54.81) and (54.82).

[7] See Eddington, equations (59.4), (58.1), (58.45) and (58.52). The additional term in λ can easily be shown necessary where the full form of equation (6) is used. Compare Einstein, l. c.

ON THE EQUILIBRIUM BETWEEN RADIATION AND MATTER IN EINSTEIN'S CLOSED UNIVERSE

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1. *Introduction.*—In two preceding articles,[1] the principles of thermodynamics have been expressed in a form suitable for applications in general relativity, and then applied to Einstein's closed universe, employing a set of coördinates in which the line element assumes the form

$$ds^2 = -R^2 d\chi^2 - R^2 \sin^2 \chi(d\theta^2 + \sin^2 \theta d\phi^2) + dt^2. \qquad (1)$$

Using these coördinates, and assuming the universe filled with a perfect fluid whose pressure is not necessarily negligible, the general relativity analogue of the first law of thermodynamics was found to lead to the equation

$$(\rho_{00} + p)V = \text{const.} \qquad (2)$$

where ρ_{00} is the *proper macroscopic* density and p the *proper* pressure of the fluid. And the analogue of the second law of thermodynamics was found to lead to the expression

$$(\phi_0 V)_{t'} - (\phi_0 V)_t \geqq 0 \qquad (3)$$

where ϕ_0 is the *proper* density of entropy of the fluid, and $\phi_0 V$ is found, as indicated, to be a quantity which can only increase with the time.

In both of these expressions V is the *proper* volume of the material in the universe as given by the expression

$$V = \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} R^3 \sin^2\chi \sin\theta d\chi d\theta\, d\phi = 2\pi^2 R^3. \tag{4}$$

Furthermore, the metrical and material properties of the universe were found to be related by the equation

$$\rho_{00} + p = \frac{1}{4\pi R^2} \tag{5}$$

which combined with equation (4) gives us

$$V = \frac{\pi^{1/2}}{4(\rho_{00} + p)^{3/2}}. \tag{6}$$

2. *Conditions of Equilibrium.*—We are now ready to consider the condition of thermodynamic equilibrium in such a universe. In accordance with equations (2) and (3), this will evidently be attained when we have the maximum possible value of $\phi_0 V$, compatible with a constant value of $(\rho_{00} + p)V$. Substituting the value of V given by equation (6), we easily find that this leads to the equations

$$\delta\phi_0 = 0 \tag{7}$$

and

$$\delta(\rho_{00} + p) = 0 \tag{8}$$

as the condition of equilibrium.

3. *Consideration of the Fluid as a Mixture of a Perfect Gas and Radiation.*—If now we consider that the fluid filling the universe is a mixture of a perfect gas and radiation, we can evidently write[2]

$$\phi_0 = Nk \log \frac{bT^{3/2}}{N} + \frac{5}{2} Nk + \frac{4}{3} aT^3 \tag{9}$$

and

$$\rho_{00} + p = Nmc^2 + \frac{5}{2} NkT + \frac{4}{3} aT^4 \tag{10}$$

where N is the number of molecules of gas per unit volume, k is Boltzmann's constant, b a constant which assures the same starting point for the entropy of gas and radiation,[2] T is the absolute temperature, a is Stefan's constant, m is the mass of one molecule and c is the velocity of light.

These expressions are functions of the concentration N and temperature T, and by performing the variations indicated by equations (7) and (8) with respect to these quantities, we have

$$\left(k \log \frac{bT^{3/2}}{N} - k + \frac{5}{2}k\right)\delta N + \left(\frac{3}{2}\frac{Nk}{T} + 4aT^2\right)\delta T = 0 \qquad (11)$$

and

$$\left(mc^2 + \frac{5}{2}kT\right)\delta N + \left(\frac{5}{2}Nk + \frac{16}{3}aT^3\right)\delta T = 0. \qquad (12)$$

Combining and rearranging, we can then solve for N in the form

$$N = bT^{3/2}\, e^{-\alpha\frac{mc^2}{kT} - \frac{5}{2}\alpha + \frac{3}{2}} \qquad (13)$$

where α has the value

$$\alpha = \frac{3/2\, Nk + 4aT^3}{5/2\, Nk + 16/3aT^3} \qquad (14)$$

and hence lies within the narrow limits

$$\frac{3}{5} < \alpha < \frac{3}{4}. \qquad (15)$$

5. *Conclusion.*—The above result for the equilibrium concentration of a perfect gas in the Einstein closed universe may be compared with the results obtained by Stern[3] and by the present writer[4] from thermodynamic considerations which in both cases tacitly assumed *flat space-time.* The writer's result was

$$N = bT^{3/2}\, e^{-\frac{mc^2}{kT}} \qquad (16)$$

and the earlier result of Stern, which led to a definite although not necessarily correct value of the constant b, was

$$N = \left(\frac{2\pi mk}{h^2}\right)^{3/2} T^{3/2}\, e^{-\frac{mc^2}{kT}}. \qquad (17)$$

Comparing equations (13), (16) and (17), and noting the limits to the possible values of α, we see that the original result of Stern and the writer, valid in flat space-time, is not greatly altered by the gravitational field in the closed universe which we have here considered. At all reasonable temperatures the concentration of molecules, even of mass as small as the electron, would still come out exceedingly small on account of the great effect of the exponential term $-mc^2/kT$, unless the constant b could be shown to have an enormous value.

This conclusion is very different from the result reached by Lenz[5] in his treatment of the equilibrium between radiation and matter in Einstein's closed universe, since he obtained even at low temperatures an approximate equality between the densities of energy in the form of gas and radiation, instead of a practical disappearance of matter. The treatment of Lenz differed from the present one in that he based it on assumed expressions for the energy and volume of the Einstein universe quite different from those that we have obtained as the natural result of our method of development. In particular, his assumption that the volume of the universe is increased by the presence of matter, but unaffected by the presence of radiation, had a great effect in favoring the production of matter. It would be of considerable interest if some logical justification could be found for such an assumption.

[1] Tolman, R. C., these PROCEEDINGS, **14**, No.3, 268–272; No.4, 348–353 (1928).

[2] If we take the entropy of a crystal as zero at the absolute zero of temperature, the entropy density of a perfect monatomic gas formed from it by vaporization is given by the Sackur-Tetrode equation

$$\phi_0 = Nk \log \left(\frac{2\pi mk}{h^2}\right)^{3/2} \frac{T^{3/2}}{N} + \frac{5}{2} Nk$$

since, however, the change in entropy in forming the crystal from radiation is unknown we must add a term Nk log (const.), to assure the same starting point as for the entropy-density expression, $4/3\ aT^3$ for radiation. This term with certain other constant factors is included in the $Nk \log b$ occurring in our expression.

[3] Stern, O., *Z. Electrochem.*, **31**, 448–449 (1925); *Trans. Farad. Soc.*, **21**, 477–478 (1925–6).

[4] Tolman, R. C., these PROCEEDINGS, **12**, 670–674 (1926).

[5] Lenz, W., *Physik. Z.*, **27**, 642–645 (1926).

PHOTOCHEMICAL OZONIZATION AND ITS RELATION TO THE POLYMERIZATION OF OXYGEN

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In an article which has been presented to the *Journal of the American Chemical Society* for publication the author has shown that the results of experiments on photochemical ozonization and on the absorption of light by oxygen afford important evidence for the existence of a polymer of the molecule O_2 in oxygen gas.

The quantitative researches of Warburg[1] have demonstrated that in oxygen gas at high pressures ozone is formed at wave-lengths 2090 Å and 2530 Å. Recent spectroscopic results[2] show, however, that the molecule O_2 does not absorb in this region. The absorption of oxygen at these wave-lengths, resulting in ozonization, is evidence that there exists in oxygen another molecular form of this element than the molecule O_2.

Furthermore, Warburg found that the conditions of ozonization at